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(71)Applicant : CHICHIBU ONODA CEMENT CORP
(72)Inventor : UZAWA MASAMI
OSONO KOICHI

(54) CONDUCTIVE SILICON CARBIDE MATERIAL COMPOSITE MATERIAL AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a SiC material composite material high in tenacity by mixing carbon or a carbon-containing compd. to a powdery mixture of the SiC and the one of more than one kind among a boride of Ti, Zr, Nb, Ta, Cr and Mo and burning the mixture.
SOLUTION: 0.5-10 pts.wt. (expressed in terms of carbon in weight) carbon or carbon-containing compd. such as phenol is added and mixed to 100 pts.wt. powdery mixture of 60-95vol% SiC powder having about $\leq 3\mu m$ grain size and 5-40vol% boride more than one kind among TiB2, ZrB2, NbB2, TaB2, CrB and MoB and having about $\leq 30\mu m$ grain size. This mixture is compacted, burned at about 1900-2300°C for about 15-60min in an inert gas atmosphere such as argon, then, the burned mater is cooled to room temp. by a speed of about 50°C/min, and a conductive SiC material composite material being a sintered body in which the boride is dispersed in a continuous SiC substrate and the carbon having a graphite structure is present in an intercrystalline phase is obtained. And the material is subjected to HIP treatment at about 1800-2000°C and about 100-2000atm pressure in an Ar gas atmosphere and the sintered body having about $\geq 95\%$ relative denseness is obtained.

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CLAIMS

[Claim(s)]
[Claim 1] Silicon carbide 60 - 95 volume %, titanium and a zirconium, niobium, a tantalum, 5-40 volume % Any one or more sorts of the boride of chromium and molybdenum in the included mixed powder 100 weight section 0.5 - 10 weight section, in addition the becoming mixture are sintered for the compound containing carbon or carbon by carbon weight conversion. Nature composite material of conductive silicon carbide characterized by being the sintered compact with which said boride phase distributes in a continuous silicon carbide base material phase, and the carbon of graphite structure exists in a grain boundary phase.
[Claim 2] Silicon carbide 60 - 95 volume %, titanium and a zirconium, niobium, a tantalum, 5-40 volume % Any one or more sorts of the boride of chromium and molybdenum in the included mixed powder 100 weight section Sinter the compound containing carbon or carbon by carbon weight conversion, and 0.5 - 10 weight section, in addition the becoming mixture are sintered at 1900-2300 degrees C. The manufacture approach of the nature composite material of conductive silicon carbide characterized by being the sintered compact with which it cools with the following cooling rates by about 50-degree-C/from this sintering temperature, and said boride phase distributes this in a continuous silicon carbide base material phase, and the carbon of graphite structure exists in a grain boundary phase.
[Claim 3] The manufacture approach of a nature composite material of conductive silicon carbide according to claim 2 characterized by sintering being pressure sintering.
[Claim 4] The manufacture approach of the nature composite material of conductive silicon carbide characterized by using inert gas as a pressure medium and carrying out HIP processing at the pressure of 1000 or more atmospheric pressures, and the temperature of 1800-2000 degrees C, without carrying out the encapsulation of the nature composite material of conductive silicon carbide produced by claim 2 or which manufacture approach of 3.

[Translation done.]

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2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the nature composite material of conductive silicon carbide which has high toughness and high intensity, and can carry out adjustable [of the resistance], and its manufacture approach.
[0002]
[Description of the Prior Art] Especially silicon carbide has attracted attention as elevated-temperature structural materials comparatively used under a harsh environment, such as an automobile engine and a gas turbine, in order to show the reinforcement and the oxidation resistance which were excellent under the elevated temperature also in the ingredient of a ceramic system. However, in order that that electric resistance may be as high as 104ohm and cm order and there may almost be no energization nature, it is cheap, and an electron discharge method with high productivity cannot be performed, but it becomes what has a quite high production cost as processing components, toughness is still quite lower in a ceramic system ingredient, this brittleness is also added, and it has been a serious failure to practical use member adaptation. On the other hand, since the metallic material had conductivity, although the electron discharge method was completed, at high temperature strength or an oxidation-resistant point, selection of the electric resistance value which becomes, and is [/ ceramic ingredients such as silicon carbide,] inferior, and can discover an ingredient was also realizable only in the range restricted extremely. For this reason, a conductive ingredient which has the mechanical property which can be stabilized and used also by hot oxidizing atmosphere which exceeds 1000 degrees C was desired.
[0003]
[Problem(s) to be Solved by the Invention] The object of this invention is offering the conductive ingredient which shows a toughness value higher than a silicon carbide sintered compact, and can give the electrical conductivity of arbitration from the electrical conductivity of the range larger than the usual metallic material, and its manufacture approach while having the high temperature strength and the oxidation resistance which cannot be acquired in a metallic material.
[0004]
[Means for Solving the Problem] this invention persons have conductivity in silicon carbide, as a result of studying many things. Also chemically, again Then, stable titanium, By considering as the compound sintered compact which deposited the carbon which is made to distribute the particle which consists of one sort chosen from the group of the boride of a zirconium, niobium, a tantalum, chromium, and molybdenum, or two sorts or more, and shows graphite structure at least to the grain boundary section The outstanding toughness and high temperature strength can be shown, and it can have high electrical conductivity, and came to complete a header and this invention for the ability of the electrical conductivity to be changed from the range of resistance larger than a common metallic material to comparatively detailed order further.
[0005] This invention Namely, silicon carbide 60 - 95 volume %, and titanium, a zirconium, 5-40 volume % Any one or more sorts of the boride of niobium, a tantalum, chromium, and molybdenum in

the included mixed powder 100 weight section 0.5 - 10 weight section, in addition the becoming mixture are sintered for the compound containing carbon or carbon by carbon weight conversion. It is the nature composite material of conductive silicon carbide characterized by being the sintered compact with which said boride phase distributes in a continuous silicon carbide base material phase, and the carbon of graphite structure exists in a grain boundary phase at least.

[0006] This invention Moreover, silicon carbide 60 - 95 volume %, and titanium, a zirconium, 5-40 volume % Any one or more sorts of the boride of niobium, a tantalum, chromium, and molybdenum in the included mixed powder 100 weight section Sinter the compound containing carbon or carbon by carbon weight conversion, and 0.5 - 10 weight section, in addition the becoming mixture are sintered at 1900-2300 degrees C. It is the manufacture approach of the nature composite material of conductive silicon carbide characterized by being the sintered compact with which it cools with the following cooling rates by about 50-degree-C/from this sintering temperature, and said boride phase distributes this in a continuous silicon carbide base material phase, and the carbon of graphite structure exists in a grain boundary phase.

[0007] Moreover, this invention is the manufacture approach of the nature composite material of conductive silicon carbide characterized by said sintering being pressure sintering.

[0008] Moreover, this invention is the manufacture approach of the nature composite material of conductive silicon carbide characterized by using inert gas as a pressure medium and carrying out HIP processing at the pressure of 1000 or more atmospheric pressures, and the temperature of 1800-2000 degrees C, without carrying out the encapsulation of the nature composite material of conductive silicon carbide produced in said which manufacture approach.

[0009]

[Embodiment of the Invention] The silicon carbide used as a raw material by this invention has desirable powder with a particle size of 3 micrometers or less from the point of the improvement in on the strength of a degree of sintering and a sintered compact, and although any of alpha mold and beta mold are sufficient as the crystal structure, since beta mold tends [comparatively] to sinter it desirably, it is good. furthermore -- although the silicon carbide powder which added the metal aluminum which is well-known sintering acid, and an aluminum oxide about 0.5 to 3% of the weight in order to raise a degree of sintering can also be used -- other impurities -- the description at the time of an elevated temperature -- since it may lead to lowering or electric resistance may be affected, it is desirable to avoid mixing. In order that a silicon dioxide may tend to generate especially powder-like silicon carbide on a front face in air, it is desirable to use what washed with hydrofluoric acid etc. in advance and removed the silicon dioxide on the front face of powder. The loadings to the raw material powder mixture of this silicon carbide are made into 60 to 95 volume %. In addition, when using the silicon carbide which added the sintering acid of metal aluminum or an aluminum oxide, it considers as the loadings of the silicon carbide containing this assistant.

[0010] The particle size is [that the purity of the boride of the titanium used as a raw material by this invention, a zirconium, niobium, a tantalum, chromium, and molybdenum should just be about 95% or more in general] desirable when being referred to as a maximum of 30 micrometers or less makes higher reinforcement and toughness give a sintered compact. The loadings to the powder mixture make any one or more sorts of said boride five to 40 volume %. Since the effectiveness of compound-izing becomes [loadings] scarce under by 5 volume % and improvement in toughness is hardly expected, it is not desirable, and since the oxidation resistance in an elevated temperature will fall if 40 volume % is exceeded, it is not desirable.

[0011] This invention is 0.5 - 10 weight ******** thing in carbon weight conversion about the compound which contains carbon or carbon in the raw material mixing powder 100 weight section containing such titanium, a zirconium, niobium, a tantalum, chromium, and any one or more sorts and the silicon carbide of the boride of molybdenum further. Although the carbon powder of crystalline substance graphite structure is desirably good as carbon which should be added here, carbon powder, such as carbon black, can also be used, for example. Furthermore, the compound with which components other than carbon contain the carbon in which decomposition balking is possible in a

heating phase as a carbon source, without using direct carbon powder may be used. As a compound containing such carbon, a phenol or its resin, tar, furan resin, etc. can be mentioned, for example. since the addition stops also being able to carry out eburnation easily while adjustment of electric resistance fine in under the 0.5 weight sections becomes difficult, it is mechanical above 10 weight sections -- since description falls, neither is desirable.

[0012] The nature composite material of conductive silicon carbide of this invention mixes the compound containing any one or more sorts and carbon, or carbon of the boride of the above silicon carbide, titanium and a zirconium, niobium, a tantalum, chromium, and molybdenum, and sinters this mixture. This sintered compact is the substantia compacta. Titanium, a zirconium, niobium, a tantalum, chromium, and any one or more sorts of particles of the boride of molybdenum in general in homogeneity and the condition of having distributed discontinuously It is firmly held in the continuous base material phase which consists of silicon carbide, and, generally the carbon of graphite structure deposits with particle size with a divisor of 10-100nm further in the grain boundary phase of silicon carbide and the metal boride which is the conductive matter. By 3 important parts of a grain boundary, the carbon which dissolution re-deposited to silicon carbide exists to several micrometer order especially. The carbon of an amorphous condition other than the crystalline substance carbon of graphite structure may be contained in such the grain boundary section at least. Being able to adjust the electric conduction property of this composite material so that it may become metal boride and the resistance of a request with carbonaceous loadings, that range is 1x103 - 106 ohm-cm in general.

[0013] Next, the detail of the manufacture approach by this invention is described. After wet blending using solvents, such as lower alcohol, and water, an acetone, adjusting the mixture which defined a raw material and its loadings like the above for example, in a ball mill and using it as desiccation granulation by spray drying etc. if needed, it fabricates in a desired configuration. As long as for example, metal mold shaping, isostatic pressing shaping (CIP) between the colds, etc. are the approaches by which the Plastic solid of high density is acquired comparatively, which shaping technique is sufficient as shaping. Subsequently, this Plastic solid is sintered. Sintering is heated for about 15 - 60 minutes at the temperature of about 1900 degrees C - 2300 degrees C in inert gas ambient atmospheres, such as an argon and helium, using the heating apparatus in which a controlled atmosphere is possible. At least 1500 degrees C of nature composite material of conductive silicon carbide of the substantia compacta can be obtained by cooling to near the room temperature more desirably with the following cooling rates by radiationnal-cooling in after [heating] furnace, or about 50-degree-C/. When the compound which contains carbon as a source of a carbon raw material here is used, in order to advance decomposition clearance of the component outside carbon smoothly, considering as an inert gas flow is desirable. In addition, since sintering cannot advance easily at the temperature of less than 1900 degrees C and the carbon of graphite structure does not generate, it is not desirable. Moreover, since it will become fault sintering and a mechanical property will deteriorate if 2300 degrees C is exceeded, it is not desirable. Moreover, since the carbon of graphite structure stops being able to deposit easily in the cooling rate with which cooling after heating of a sintered compact exceeds a part for about 50-degree-C/, it is not desirable.

[0014] In the manufacture approach of this invention, although the pressure at the time of said sintering can respond also before and behind ordinary pressure, i.e., 1 atmospheric pressure, in order to obtain more high intensity and the nature composite material of conductive silicon carbide which has high ****, it is good to perform pressure sintering preferably. The approach (the capsule HIP method) of sintering the calcinated object enclosed with capsules, such as well-known hot pressing and glass, as the approach of such pressure sintering, for example by the isostatic pressing between heat can be mentioned.

[0015] moreover -- like the above -- end ordinary pressure or the relative density which carried out pressure sintering -- about 95% or more of sintered compact -- more -- high -- in order to consider as the thing of precise and more homogeneous description, without enclosing in capsules, such as glass, HIP processing of the element assembly is directly carried out in an argon pressure medium with the temperature of about 1800 degrees C - 2000 degrees C, and 1000 to pressure 2000 atmospheric pressure,

namely, capsule free HIP processing can also be carried out. In addition, since the grain growth connected with lowering on the strength will be seen and the effectiveness of HIP processing will hardly be seen at less than 1800 degrees C if the temperature of HIP processing exceeds 2000 degrees C, it is not desirable. Similarly, since the effectiveness of HIP processing of even less than 1000 atmospheric pressure even of pressures is hardly seen, it is not desirable.

[0016]

[Function] Metal boride particles, such as zirconium boride which constitutes the nature composite material of this conductive silicon carbide, can improve the toughness value of an ingredient substantially by the principle of a particle-dispersion reinforcement while it distributes to homogeneity and they give electrical conductivity higher than a common metallic material into a silicon carbide matrix. Moreover, the carbon in the nature composite material of this conductive silicon carbide exists mainly by the so-called amorphous condition and the dimorphism voice of the graphite crystal structure, and the former shows a sintering acid-operation and contributes to sintering of a silicon carbide base material. The resistance value change corresponding to change of the loadings to on the other hand resistance changing [metal boride] substantially according to change of the minute amount of the loadings, as for the latter is quite loose. Thus, carbon can produce what it adjusted comparatively strictly to order with the fine value although the resistance adjustment function could produce that in which the nature composite-material boride of this conductive silicon carbide so has desired resistance from the resistance range where width of face is wider than a metal unlike metal boride.

[0017]

[Example]

[Example 1] beta mold silicon carbide with a mean particle diameter of 0.5 micrometers which carried out washing processing beforehand with hydrofluoric acid (SiC), The titanium boride whose diameter of a centriole is 2.8 micrometers in the particle size of 4 micrometers or less (TiB2), The zirconium boride whose diameter of a centriole is 2.1 micrometers in the particle size of 5 micrometers or less (ZrB2), The boronizing niobium whose diameter of a centriole is 2.3 micrometers in the particle size of 5 micrometers or less (NbB2), The boronizing tantalum whose diameter of a centriole is 2.2 micrometers in the particle size of 5 micrometers or less (TaB2), The mixture of the blending ratio of coal described in a table 1 using the boronizing molybdenum (MoB) whose diameter of a centriole is 3.0 micrometers in the particle size of 4 micrometers or less, the boronizing chromium (CrB) whose diameter of a centriole is 2.9 micrometers in the particle size of 4 micrometers or less, and a phenol (C6H5OH) was produced by ball mill mixing. Fabricating this mixture with metal mold shaping, respectively, sintering was performed at 2200 degrees C for 20 minutes using the electric furnace among the argon air current adjusted so that it might become about 1.0 to 1.1 atmospheric pressure, it cooled to about 300 degrees C with about 15-degree-C cooling rate for /, and each Plastic solid produced the sintered compact (this invention article 1-12) of the substantia compacta by cooling radiationally in a furnace to about 25 degrees C after that.

[0018]

[A table 1]

		混合物配合量（Kg）			曲げ強度（MPa）		破壊靱性	相対密度	電気抵抗
		SiC	硼化物種・量	フェノール	常温	1000℃	$MPa \cdot m^{1/2}$	%	Ω·cm
	本発明品1	2.761	TiB_2・0.630	0.035	570	550	4.3	98	30
	本発明品2	1.290	ZrB_2・0.401	0.066	580	540	4.7	98	50
実	本発明品3	1.926	ZrB_2・2.436	0.098	590	580	5.3	97	0.05
	本発明品4	3.050	ZrB_2・0.305	0.155	600	600	4.2	97	1500
施	本発明品5	1.290	ZrB_2・0.401	0.017	620	610	4.3	97	300
	本発明品6	1.290	ZrB_2・0.401	0.338	570	570	4.8	97	0.02
例	本発明品7	3.050	ZrB_2・0.305	0.137	610	620	4.1	98	2000
	本発明品8	1.926	ZrB_2・2.436	0.152	590	590	5.7	97	0.008
1	本発明品9	2.729	NbB_2・1.041	0.057	600	600	4.4	97	500
	本発明品10	2.729	TaB_2・1.673	0.088	630	630	4.2	97	90
	本発明品11	2.568	CrB・1.234	0.057	650	650	4.7	98	300
	本発明品12	2.600	MoB・0.644	0.085	590	570	4.4	97	70

[0019] The obtained sintered compact measured the flexural strength (MPa) in the inside of ordinary temperature (about 25 degrees C) and 1000-degree C atmospheric air, the fracture toughness (MPa-m 1/2) in ordinary temperature, relative density (%), and the electric resistance (ohm-cm) in ordinary temperature. The value is described according to a table 1. in addition, SEPB to which fracture toughness was based on JIS-R1607 in the three-point bending reinforcement by the approach by which flexural strength was based on JIS-R1601 -- law -- it is -- relative density -- Archimedes -- it is law and electric resistance was measured by 4 terminal method, respectively. Moreover, when the crystal phase was investigated by the X diffraction and Raman spectroscopic analysis, any sintered compact checked existence of any one sort and the beta mold SiC of TiB2, ZrB2, NbB2, TaB2, MoB, and CrB, and graphite mold carbon.

[0020] [Example 2] Ball mill mixing adjusted 0.40kg of zirconium borides whose diameter of a centriole is 2.1 micrometers, and the mixture which consists of carbon black 0.063kg with beta mold silicon carbide with a mean particle diameter of 0.5 micrometers which carried out washing processing beforehand with hydrofluoric acid of 1.29kg, and the particle size of 5 micrometers or less, and the Plastic solid was produced by carrying out metal mold shaping of this. It sintered on the conditions which described this Plastic solid in a table 2 by the capsule HIP method by the HIP equipment using the electric furnace of the same argon air-current ambient atmosphere as said example 1, the hotpress furnace under argon atmosphere, or an argon pressure medium, and cooled from each sintering maximum temperature to about 300 degrees C with 50-degree-C cooling rate for /, and the sintered compact (this invention article 13-16) of the substantia compacta was produced by cooling radiationally in a furnace to ordinary temperature after that. The obtained sintered compact is the same approach as said example 1, and measured the flexural strength in the inside of ordinary temperature (about 25 degrees C) and 1000-degree C atmospheric air, the fracture toughness in ordinary temperature, relative density, and the electric resistance in ordinary temperature. The value is described according to a table 2. Moreover, when the crystal phase was investigated by the X diffraction and Raman spectroscopic analysis, any sintered compact checked existence of ZrB2, the beta mold SiC, and graphite mold carbon.

[0021]

[A table 2]

		焼結温度	焼結圧力	焼結方法	曲げ強度（MPa）		破壊靭性	相対密度	電気抵抗
		℃	MPa		常温	1000℃	$MPa \cdot m^{1/2}$	%	Ω•cm
実施例2	本発明品13	1900	−	常圧焼結	590	580	4.4	98	50
	本発明品14	2300	−	常圧焼結	550	540	4.3	97	50
	本発明品15	2000	30	ﾎｯﾄﾌﾟﾚｽ法	650	600	4.7	99	60
	本発明品16	2000	200	ｶﾌﾟｾﾙHIP	690	610	4.8	99	60

[0022] [Example 3] The sintered compact which was produced in said example 2 and which becomes this invention article 13 was directly installed into HIP equipment, without carrying out an encapsulation, and by the capsule free HIP method, HIP processing was carried out at 1000 atmospheric pressures and 1800 degrees C with the argon pressure medium for 30 minutes, and it cooled on the same conditions as said example 1. The toughness and conductivity in which the flexural strength in the inside of ordinary temperature atmospheric air of the flexural strength in the inside of 680MPa and 1000-degree C atmospheric air is electric resistance 3.1x102 ohm-cm in 660MPa(s), 99% of relative density, and fracture toughness 4.7 MPa-m1/2 ordinary temperature in ordinary temperature, and each weighted solidity measured by the same approach as the example 1 of the obtained sintered compact was excellent were shown. Moreover, when the crystal phase of this sintered compact was investigated by the X diffraction and Raman spectroscopic analysis, existence of ZrB2, the beta mold SiC, and graphite mold carbon was checked.

[0023] [Example 1 of a comparison] Ball mill mixing adjusted 0.24kg of zirconium borides whose diameter of a centriole is 2.1 micrometers, and the mixture which consists of carbon black 0.06kg with beta mold silicon carbide with a mean particle diameter of 0.5 micrometers which carried out washing processing beforehand with hydrofluoric acid of 3.08kg, and the particle size of 5 micrometers or less, and the Plastic solid was produced by carrying out metal mold shaping of this. The sintered compact was produced for this Plastic solid on the same sintering and cooling conditions with it being the same as that of said example 1. Each weighted solidity measured by the same approach as the example 1 of the obtained sintered compact became flexural strength 420MPa in the inside of ordinary temperature atmospheric air, flexural strength 400MPa in the inside of 1000-degree C atmospheric air, 96% of relative density, fracture toughness 3.9 MPa-m 1/2 in ordinary temperature, and electric resistance 20000 ohm-cm in ordinary temperature, and its electric resistance was high and it became conductivity with the scarce thing.

[0024] [Example 2 of a comparison] Ball mill mixing adjusted 1.21kg of zirconium borides whose diameter of a centriole is 2.1 micrometers, and the mixture which consists of carbon black 0.004kg with beta mold silicon carbide with a mean particle diameter of 0.5 micrometers which carried out washing processing beforehand with hydrofluoric acid of 2.56kg, and the particle size of 5 micrometers or less, and the Plastic solid was produced by carrying out metal mold shaping of this. The sintered compact was produced for this Plastic solid on the same sintering and cooling conditions with it being the same as that of said example 1. The weighted solidity measured by the same approach as the example 1 of the obtained sintered compact became flexural strength 210MPa in the inside of ordinary temperature atmospheric air, and 91% of relative density, and became what lacks in compactness remarkably.

[0025]

[Effect of the Invention] the nature composite material of conductive silicon carbide of this invention raised the toughness of silicon carbide substantially, and it excelled also in the elevated temperature comparatively -- mechanical -- it is stabilized, and description can be shown and it has good electrical conductivity. This electrical conductivity can produce what has the electrical conductivity of arbitration from the range of electrical conductivity larger than a metallic material with high degree of accuracy by

the process of this invention. From such a description, the composite material of this invention may be utilizable enough also as functional material, such as a resistor which serves as high temperature other than the activity as a structural element comparatively, an electric fuse, and a thermo sensor.

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TECHNICAL FIELD

[The technical field to which invention belongs] This invention relates to the nature composite material of conductive silicon carbide which has high toughness and high intensity, and can carry out adjustable [of the resistance], and its manufacture approach.

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PRIOR ART

[Description of the Prior Art] Especially silicon carbide has attracted attention as elevated-temperature structural materials comparatively used under a harsh environment, such as an automobile engine and a gas turbine, in order to show the reinforcement and the oxidation resistance which were excellent under the elevated temperature also in the ingredient of a ceramic system. However, in order that that electric resistance may be as high as 104ohm and cm order and there may almost be no energization nature, it is cheap, and an electron discharge method with high productivity cannot be performed, but it becomes what has a quite high production cost as processing components, toughness is still quite lower in a ceramic system ingredient, this brittleness is also added, and it has been a serious failure to practical use member adaptation. On the other hand, since the metallic material had conductivity, although the electron discharge method was completed, at high temperature strength or an oxidation-resistant point, selection of the electric resistance value which becomes, and is [/ ceramic ingredients such as silicon carbide,] inferior, and can discover an ingredient was also realizable only in the range restricted extremely. For this reason, a conductive ingredient which has the mechanical property which can be stabilized and used also by hot oxidizing atmosphere which exceeds 1000 degrees C was desired.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention is offering the conductive ingredient which shows a toughness value higher than a silicon carbide sintered compact, and can give the electrical conductivity of arbitration from the electrical conductivity of the range larger than the usual metallic material, and its manufacture approach while having the high temperature strength and the oxidation resistance which cannot be acquired in a metallic material.

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MEANS

[Means for Solving the Problem] this invention persons have conductivity in silicon carbide, as a result of studying many things. Also chemically, again Then, stable titanium, By considering as the compound sintered compact which deposited the carbon which is made to distribute the particle which consists of one sort chosen from the group of the boride of a zirconium, niobium, a tantalum, chromium, and molybdenum, or two sorts or more, and shows graphite structure at least to the grain boundary section The outstanding toughness and high temperature strength can be shown, and it can have high electrical conductivity, and came to complete a header and this invention for the ability of the electrical conductivity to be changed from the range of resistance larger than a common metallic material to comparatively detailed order further.
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[0009]
[Embodiment of the Invention] The silicon carbide used as a raw material by this invention has desirable powder with a particle size of 3 micrometers or less from the point of the improvement in on the strength of a degree of sintering and a sintered compact, and although any of alpha mold and beta mold are sufficient as the crystal structure, since beta mold tends [comparatively] to sinter it desirably, it is good. furthermore -- although the silicon carbide powder which added the metal aluminum which is

well-known sintering acid, and an aluminum oxide about 0.5 to 3% of the weight in order to raise a degree of sintering can also be used -- other impurities -- the description at the time of an elevated temperature -- since it may lead to lowering or electric resistance may be affected, it is desirable to avoid mixing. In order that a silicon dioxide may tend to generate especially powder-like silicon carbide on a front face in air, it is desirable to use what washed with hydrofluoric acid etc. in advance and removed the silicon dioxide on the front face of powder. The loadings to the raw material powder mixture of this silicon carbide are made into 60 to 95 volume %. In addition, when using the silicon carbide which added the sintering acid of metal aluminum or an aluminum oxide, it considers as the loadings of the silicon carbide containing this assistant.

[0010] The particle size is [that the purity of the boride of the titanium used as a raw material by this invention, a zirconium, niobium, a tantalum, chromium, and molybdenum should just be about 95% or more in general] desirable when being referred to as a maximum of 30 micrometers or less makes higher reinforcement and toughness give a sintered compact. The loadings to the powder mixture make any one or more sorts of said boride five to 40 volume %. Since the effectiveness of compound-izing becomes [loadings] scarce under by 5 volume % and improvement in toughness is hardly expected, it is not desirable, and since the oxidation resistance in an elevated temperature will fall if 40 volume % is exceeded, it is not desirable.

[0011] This invention is 0.5 - 10 weight ******** thing in carbon weight conversion about the compound which contains carbon or carbon in the raw material mixing powder 100 weight section containing such titanium, a zirconium, niobium, a tantalum, chromium, and any one or more sorts and the silicon carbide of the boride of molybdenum further. Although the carbon powder of crystalline substance graphite structure is desirably good as carbon which should be added here, carbon powder, such as carbon black, can also be used, for example. Furthermore, the compound with which components other than carbon contain the carbon in which decomposition balking is possible in a heating phase as a carbon source, without using direct carbon powder may be used. As a compound containing such carbon, a phenol or its resin, tar, furan resin, etc. can be mentioned, for example. since the addition stops also being able to carry out eburnation easily while adjustment of electric resistance fine in under the 0.5 weight sections becomes difficult, it is mechanical above 10 weight sections -- since description falls, neither is desirable.

[0012] The nature composite material of conductive silicon carbide of this invention mixes the compound containing any one or more sorts and carbon, or carbon of the boride of the above silicon carbide, titanium and a zirconium, niobium, a tantalum, chromium, and molybdenum, and sinters this mixture. This sintered compact is the substantia compacta. Titanium, a zirconium, niobium, a tantalum, chromium, and any one or more sorts of particles of the boride of molybdenum in general in homogeneity and the condition of having distributed discontinuously It is firmly held in the continuous base material phase which consists of silicon carbide, and, generally the carbon of graphite structure deposits with particle size with a divisor of 10-100nm further in the grain boundary phase of silicon carbide and the metal boride which is the conductive matter. By 3 important parts of a grain boundary, the carbon which dissolution re-deposited to silicon carbide exists to several micrometer order especially. The carbon of an amorphous condition other than the crystalline substance carbon of graphite structure may be contained in such the grain boundary section at least. Being able to adjust the electric conduction property of this composite material so that it may become metal boride and the resistance of a request with carbonaceous loadings, that range is 1x103 - 106 ohm-cm in general.

[0013] Next, the detail of the manufacture approach by this invention is described. After wet blending using solvents, such as lower alcohol, and water, an acetone, adjusting the mixture which defined a raw material and its loadings like the above for example, in a ball mill and using it as desiccation granulation by spray drying etc. if needed, it fabricates in a desired configuration. As long as for example, metal mold shaping, isostatic pressing shaping (CIP) between the colds, etc. are the approaches by which the Plastic solid of high density is acquired comparatively, which shaping technique is sufficient as shaping. Subsequently, this Plastic solid is sintered. Sintering is heated for about 15 - 60 minutes at the temperature of about 1900 degrees C - 2300 degrees C in inert gas ambient atmospheres, such as an

argon and helium, using the heating apparatus in which a controlled atmosphere is possible. At least 1500 degrees C of nature composite material of conductive silicon carbide of the substantia compacta can be obtained by cooling to near the room temperature more desirably with the following cooling rates by radiationnal-cooling in after [heating] furnace, or about 50-degree-C/. When the compound which contains carbon as a source of a carbon raw material here is used, in order to advance decomposition clearance of the component outside carbon smoothly, considering as an inert gas flow is desirable. In addition, since sintering cannot advance easily at the temperature of less than 1900 degrees C and the carbon of graphite structure does not generate, it is not desirable. Moreover, since it will become fault sintering and a mechanical property will deteriorate if 2300 degrees C is exceeded, it is not desirable. Moreover, since the carbon of graphite structure stops being able to deposit easily in the cooling rate with which cooling after heating of a sintered compact exceeds a part for about 50-degree-C/, it is not desirable.

[0014] In the manufacture approach of this invention, although the pressure at the time of said sintering can respond also before and behind ordinary pressure, i.e., 1 atmospheric pressure, in order to obtain more high intensity and the nature composite material of conductive silicon carbide which has high ****, it is good to perform pressure sintering preferably. The approach (the capsule HIP method) of sintering the calcinated object enclosed with capsules, such as well-known hot pressing and glass, as the approach of such pressure sintering, for example by the isostatic pressing between heat can be mentioned.

[0015] moreover -- like the above -- end ordinary pressure or the relative density which carried out pressure sintering -- about 95% or more of sintered compact -- more -- high -- in order to consider as the thing of precise and more homogeneous description, without enclosing in capsules, such as glass, HIP processing of the element assembly is directly carried out in an argon pressure medium with the temperature of about 1800 degrees C - 2000 degrees C, and 1000 to pressure 2000 atmospheric pressure, namely, capsule free HIP processing can also be carried out. In addition, since the grain growth connected with lowering on the strength will be seen and the effectiveness of HIP processing will hardly be seen at less than 1800 degrees C if the temperature of HIP processing exceeds 2000 degrees C, it is not desirable. Similarly, since the effectiveness of HIP processing of even less than 1000 atmospheric pressure even of pressures is hardly seen, it is not desirable.

[Translation done.]

OPERATION

[Function] Metal boride particles, such as zirconium boride which constitutes the nature composite material of this conductive silicon carbide, can improve the toughness value of an ingredient substantially by the principle of a particle-dispersion reinforcement while it distributes to homogeneity and they give electrical conductivity higher than a common metallic material into a silicon carbide matrix. Moreover, the carbon in the nature composite material of this conductive silicon carbide exists mainly by the so-called amorphous condition and the dimorphism voice of the graphite crystal structure, and the former shows a sintering acid-operation and contributes to sintering of a silicon carbide base material. The resistance value change corresponding to change of the loadings to on the other hand resistance changing [metal boride] substantially according to change of the minute amount of the loadings, as for the latter is quite loose. Thus, carbon can produce what it adjusted comparatively strictly to order with the fine value although the resistance adjustment function could produce that in which the nature composite-material boride of this conductive silicon carbide so has desired resistance from the resistance range where width of face is wider than a metal unlike metal boride.

[Translation done.]